Chapter 3

Results & Discussion
PVC doped with Li^+ salts

3.0 RESULTS & DISCUSSION OF PVC DOPED WITH Li^+ SALTS

The films prepared by adding different amounts of $LiClO_4$ to PVC appeared whitish and opaque. They were soft, rubbery and flexible with a smooth surface. The pure PVC film was transparent and colorless.

3.1 AC Conductivity Analysis

From the impedance measurement that gives frequency f_r, impedance Z, and phase angle θ values, Z $\sin\theta$ and Z $\cos\theta$, i.e., the imaginary and real parts of impedance were calculated, and the Cole-Cole plots were plotted. The Cole-Cole plot for pure PVC is shown in figure[3.1]. From the plots, the bulk resistance, R_b, is estimated and this value is used to calculate the a.c conductivity value at room temperature using the equation $\sigma=L/R_bA$, where L is the thickness of the film and A is the film area and σ is the electrical conductivity. Figures [3.2] to [3.5] shows Cole-Cole plots for PVC doped with lithium salts. Compared to pure PVC samples, the doped samples show a slight increase of an order in magnitude of conductivity.

Generally, the shape of the impedance plots that were obtained can be equaled to an equivalent circuit, which contains in series a resistor and a capacitor and the same in parallel. A more complicated network of resistor and capacitors can represent the cell, which is called the equivalent circuit. The impedance plot will give equivalent circuit that could be due to bulk capacitance, grain boundaries and electrode contact [63-65].

The conductivity of pure PVC is in the order of 10^{-8} S/cm. The conductivity values for the doped samples of PVC were found to be as given in the table[3.1].

Table[3.1]: Table listing out the concentration of polymer, salt, solvent, thickness of the film and conductivity.

Sl. No	PVC (Wt %)g	$LiClO_4$ (Wt %)g	THF (ml)	Thickness (cms)	Conductivity (S/cm)
1	0.50	-	30	0.0040	5.60×10^{-8}
2	0.40	0.10	30	0.0045	1.04×10^{-7}
3	**0.35**	**0.15**	**30**	**0.0030**	$\mathbf{1.63 \times 10^{-7}}$
4	0.30	0.20	30	0.0045	1.21×10^{-7}
5	0.25	0.25	30	0.0035	1.01×10^{-7}

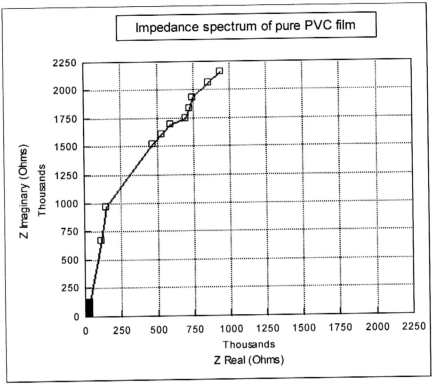
The variation of the slope of the curve in the sample is expected to be resulting from the roughness of electrode interface. It has been observed that [66-68] partial crystallanity in polymer electrolytes leads to depressed and skewed semicircles. This shows that the material has several relaxation times and not a single relaxation time as in Debye type materials. This phenomenon can also be seen with the present samples. The best conductivity concentration for lithium doped among the samples studied was the sample with ratio of 70wt % PVC : 30wt % Salt.

Figure [3.6] shows the variation of conductivity with the amount of $LiClO_4$ added. It can be seen that the electrical conductivity of the $LiClO_4$ added film seems to increase quite linearly with the salt concentration (upto 0.15g), and seems to agree with the weak electrolyte theory. However when the amount of dopant exceeds this value, σ seems to increase at a decreasing rate until a maximum is reached, i.e., until 0.25g of dopant was added. The ionic conductivity σ, is generally expressed as

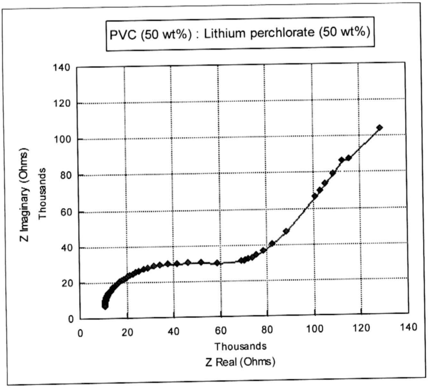
$$\sigma = nze\mu \qquad (1)$$

where n, z and μ are respectively the number, valence and mobility of the charge carriers. The charge mobility μ is assumed constant and the electrical conductivity is proportional to the concentration of free ions. [69-71]. If the weak electrolyte theory is applicable in this case, then the electrical conductivity should vary linearly with the dopant concentration as shown by the dotted line in figure [3.6]. The decrease in the increasing rate of σ and finally the decrease in σ observed, reflects a decrease in the number of free ions. This can be attributed to the inability of the fixed volume of the PVC host to assimilate all the free ions, which resulted from the assumingly weak dissociation of $LiClO_4$. This decreases the number of free ions and lead to the decrease in electrical conductivity, σ, according to the weak electrolyte theory.

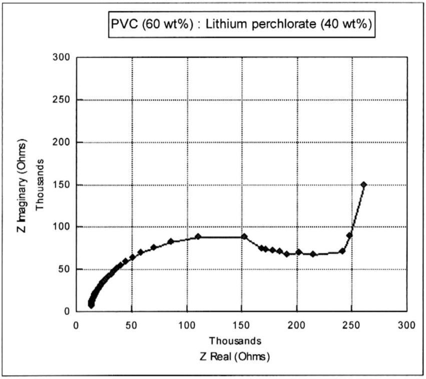
Another way this situation can be looked at, is to assume that all the lithium and perchlorate ions are assimilated into the PVC host, but the fixed volume of the host material and the increasing number of ions that are supposed to be free caused severe overcrowding. The severe overcrowding could lead to more ions being immobilized which eventually leads to the corresponding decrease in the actual number of free ions and to the drop in σ [72].



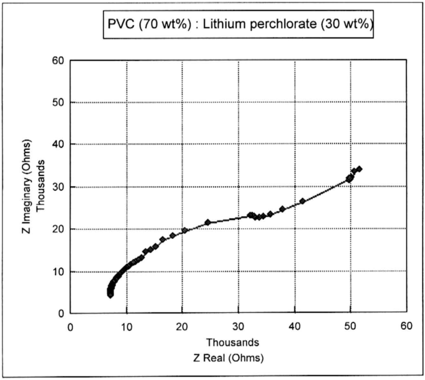
Fig[3.1]: Impedance spectrum of pure PVC film (R_b=22727Ω)



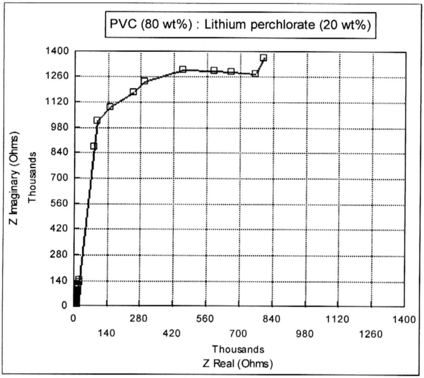
Fig[3.2]: Impedance spectrum of PVC film doped with $LiClO_4$ (R_b=10949Ω)



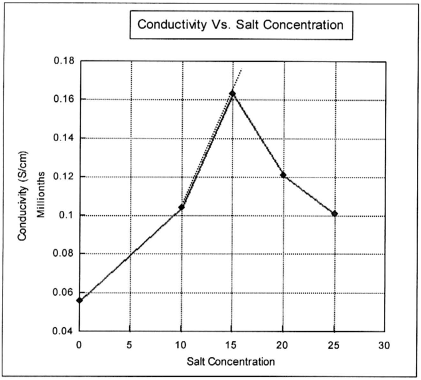
Fig[3.3]: Impedance spectrum of PVC film doped with $LiClO_4$ (R_b=11764Ω)



Fig[3.4]: Impedance spectrum of PVC film doped with $LiClO_4$ (R_b=5857Ω)



Fig[3.5]: Impedance spectrum of PVC film doped with $LiClO_4$ (R_b=13658Ω)



Fig[3.6]: Graph depicting conductivity against salt concentration

Other salts were added to PVC to compare their performance with that of $LiClO_4$. In the earlier attempt it was seen that, highest conductivity was achieved with the concentration of 70 wt% PVC with 30 wt% $LiClO_4$. Table [3.2] lists out the salts and the corresponding electrical conductivity values achieved with them.

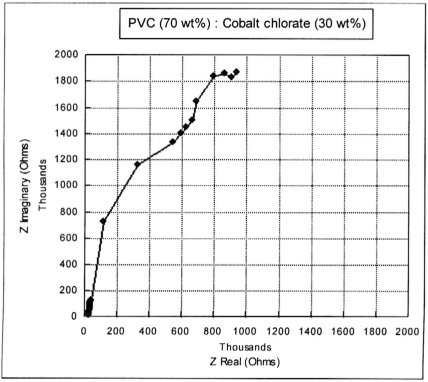
Table[3.2]: Table listing out the salts, their bulk resistance, thickness and conductivity values.

Sl. No.	Salt	Bulk Resistance-R_b (Ω)	Thickness (cms)	Conductivity (S/cms)
1	Cobalt chlorate	25000	0.0050	6.36×10^{-8}
2	Lithium Iodide	20588	0.0050	7.73×10^{-8}
3	Lithium Triflate	11200	0.0045	1.27×10^{-7}
4	Lithium Trifloroborate	6000	0.0030	1.59×10^{-7}

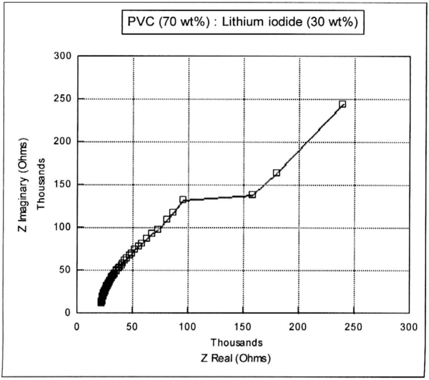
Figures [3.7] to [3.10] gives the impedance spectrum of PVC with other salts. It is found that $LiClO_4$ gives the best conductivity amongst them. However, it can be noticed, that $LiCF_3SO_3$ and $LiBF_4$ do give conductivities very near to that of $LiClO_4$. Nature of salt does influence the conductivity of the polymer salt complexes. For a given concentration of the salt, the concentration of ionic charge carriers in the electrolyte is determined by the dielectric constant of the polymer and the lattice energy of the salt.

Polymers with high dielectric constants and salts having low lattice energies generally are expected to promote greater dissociation of the salt, thereby providing higher concentrations of ions. The lithium salts used to for Li^+ conductive polymer electrolytes have large anions and low lattice energie such as $LiClO_4$, $LiBF_4$ and $LiCF_3SO_3$, promote high conductivity compared with the halides such as LiCl, LiI and LiBr, which have relatively high lattice energies [73]. Hence, $LiBF_4$ and $LiCF_3SO_3$ give conductivities very near to that of $LiClO_4$. Further research can be done with these salts and test their ability to improve upon the existing conductivities when mixed with plasticizers.

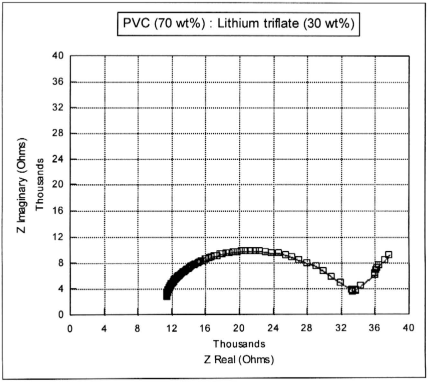
In this respect, polymer electrolytes behave like organic liquid electrolytes. Dissolution of Li salt in a polymer occurs when the solvation energy of the polymer with Li^+ is large enough to overcome te latter energy of the salt. When the anions are large, as in the case of complex ions, substantial delocalization of the negative charge occurs with the reduction of ion-ion interactions. The consequence is increase in conductivity [74].



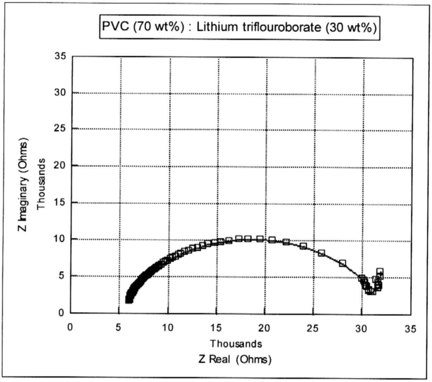
Fig[3.7]: Impedance spectrum of PVC doped with $CoCl_2$ (R_b=25000Ω)



Fig[3.8]: Impedance spectrum of PVC doped with LiI (R_b=20588Ω)



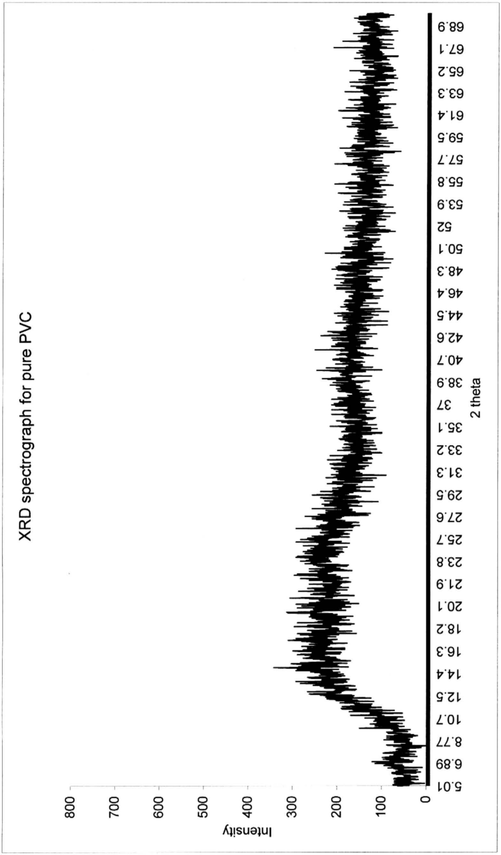
Fig[3.9]: Impedance spectrum of PVC doped with $LiCF_3SO_3$(R_b=11047Ω)



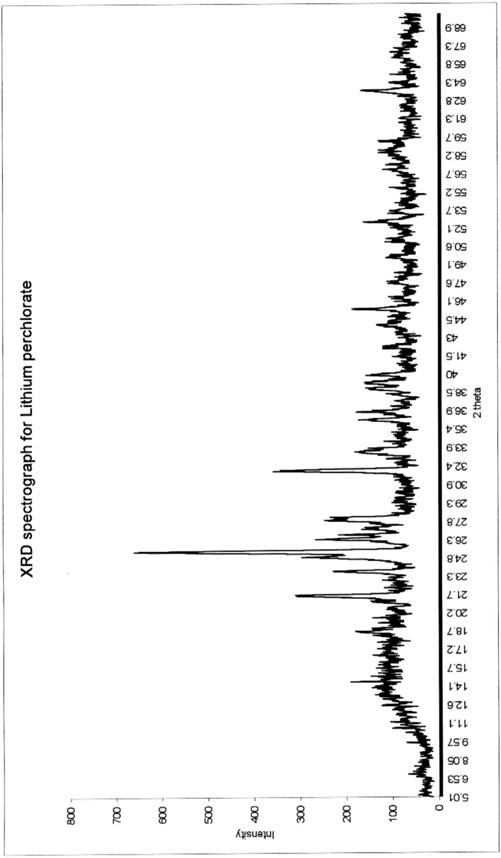
Fig[3.10]: Impedance spectrum of PVC doped with $LiBF_4(R_b=6000\Omega)$

3.2 XRD Analysis

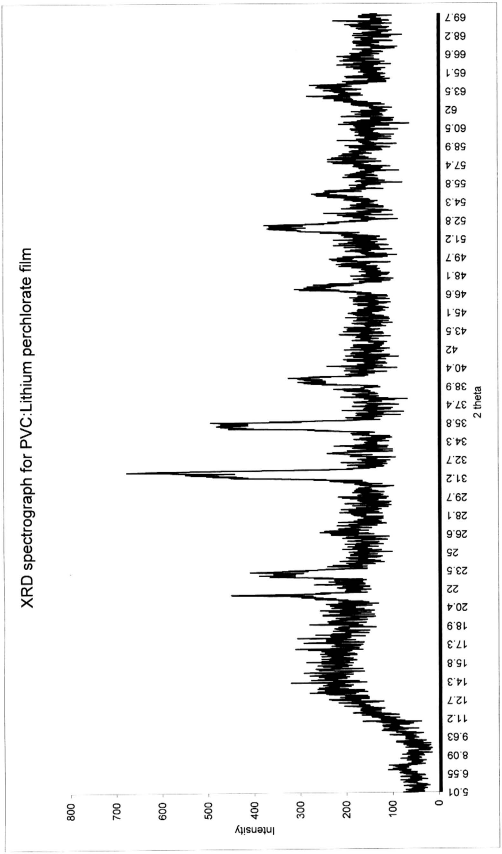
Figures [3.11] to [3.13] give the structural morphology of the polymer PVC, salt $LiClO_4$ and highest conducting film with a concentration of 70 wt% PVC and 30 wt% salt. PVC being partially syndiotactic, exhibits an amorphous structure. $LiClO_4$ is crystalline in nature and the polymer film exhibits amorphous nature but does have some degree of crystallanity in it. It can be seen in the form of peaks. This also explains the reason for a low conductivity. It can be seen that the conductivity of pure PVC and that of this film differs by just one order. It also tends to prove that some percentage of complexity has taken place between the polymer and the salt.



Fig[3.11]: XRD of pure PVC



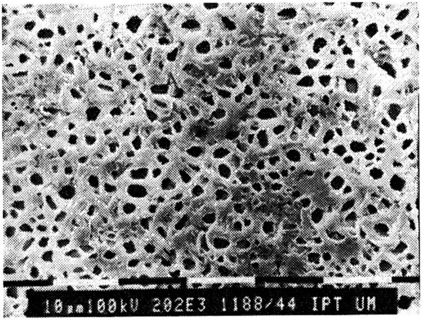
Fig[3.12]: XRD of $LiClO_4$



Fig[3.13]: XRD of electrolyte film- PVC complexed with $LiClO_4$

3.3 SEM Analysis

SEM was carried out to study the surface structure and morphology of the complexed PVC. SEM Micrographs of PVC-$LiClO_4$ complexed at 70 wt% and 30 wt% respectively can be seen in figures [3.14] to 3.16] at different levels of magnification. It can be seen from the given figures that the surface of the polymer is not smooth and has lot of pores in it. And because of these pores or grains, which are quite big, the ions have to move along their boundary. Hence, we can notice that the conductivity of pure PVC and that of this particular film differs only by one degree.



Fig[3.14]: SEM Micrograph of the polymer electrolyte film (magnification – 2000)

3.4 EDAX Analysis

EDAX analysis was done to find out whether there existed any other impurities which were instrumental in improving the conductivity. However none were found. The graph showed only one peak belonging to the chlorine of the PVC chain. It was already known that lithium cannot be seen on the graph because of it low atomic weight, and hence we can see only that of chlorine, as shown in figure [3.17].

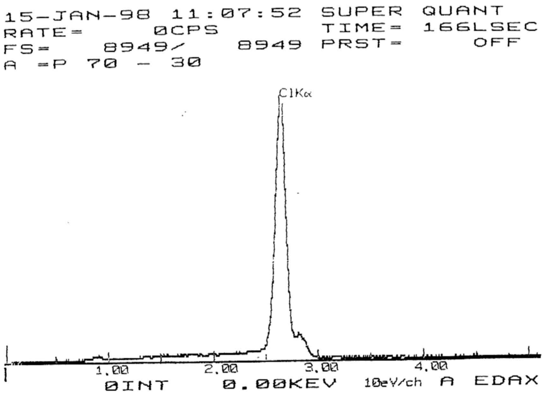


Fig [3.17]: EDAX of polymer-salt complex with weight ratio of 70:30 respectively.